

**This Page Is Inserted by IFW Operations
and is not a part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- **BLACK BORDERS**
- **TEXT CUT OFF AT TOP, BOTTOM OR SIDES**
- **FADED TEXT**
- **ILLEGIBLE TEXT**
- **SKEWED/SLANTED IMAGES**
- **COLORED PHOTOS**
- **BLACK OR VERY BLACK AND WHITE DARK PHOTOS**
- **GRAY SCALE DOCUMENTS**

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PCT

CON. US 5,378,671
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C10G 47/20, B01J 29/06, 37/00	A1	(11) International Publication Number: WO 94/29408 (43) International Publication Date: 22 December 1994 (22.12.94)
(22) International Application Number: PCT/US94/05331 (22) International Filing Date: 16 May 1994 (16.05.94) (30) Priority Data: 070,822 3 June 1993 (03.06.93) US (71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US). (72) Inventors: KEVILLE, Kathleen, Marie; 7020 Westgate Drive, Beaumont, TX 77706 (US). TIMKEN, Hye, Kyung, Cho; 44 N. Girard Street, Woodbury, NJ 08096 (US). WARE, Robert, Adam; 8055 Stenton Avenue, Wyndmoor, PA 19118 (US). (74) Agents: ROBERTS, Peter, W. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).		(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR PREPARING AN ALUMINA BOUND ZEOLITE CATALYST (57) Abstract In a process for preparing an alumina bound, zeolite catalyst, a zeolite of low silanol content is used as the source of zeolite used to prepare the catalyst. A particular zeolite used in this catalyst is zeolite Y. This catalyst may be combined with at least one hydrogenation component and used to hydrocrack hydrocarbons, such as gas oils. In particular, an NiW/USY/alumina catalyst may be used in a hydrocracking reaction to produce distillate boiling range hydrocarbons from higher boiling hydrocarbons.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

PROCESS FOR PREPARING AN ALUMINA BOUND ZEOLITE CATALYST

This invention relates to a process for preparing an alumina bound, zeolite catalyst useful in hydrocracking hydrocarbons, such as gas oils.

5 Hydrocracking is a versatile petroleum refining process which enjoys widespread use in the refining industry. Hydrocracking has the ability to process a wide range of difficult feedstocks into a variety of desirable products. Feedstocks which may be treated by this process
10 include heavy naphthas, kerosenes, refractory catalytically cracked cycle stocks and high boiling virgin and coker gas oils. At high severities, hydrocracking can convert these materials to gasoline and lower boiling paraffins; lesser severities permit the higher boiling feedstocks to be
15 converted into lighter distillates such as diesel fuels and aviation kerosenes.

Hydrocracking is conventionally carried out at moderate temperatures of 350°C to 450°C (650°F to 850°F), because the thermodynamics of the hydrocracking process
20 become unfavorable at higher temperatures. In addition, high hydrogen pressures, usually at least 5600 kPa (800 psig) are required to prevent catalyst aging and so to maintain sufficient activity to enable the process to be operated with a fixed bed of catalyst for periods of one to
25 two years without the need for regeneration.

The catalysts used for hydrocracking usually comprise a transition metal such as nickel, cobalt, tungsten or molybdenum on an acidic support such as alumina or silica-alumina although noble metals such as platinum may also be
30 used. Combinations of metals such as nickel with tungsten have been found to be extremely effective with a wide variety of feedstocks as has the presulfiding technique which is now widely employed.

Hydrocracking processes using the hydrogen form of
35 zeolite Y as the acidic component are described, for example, in U.S. Pat. Nos. 3,269,934 and 3,524,809, and in

"Preparation of Catalysts III", ed. by G. Poncelet, P. Grange, and P.A. Jacobs, Elsevier Science Publishers, 587 (1983).

5 High silica/alumina ratio zeolites have been shown to be the preferred catalysts for many hydrocarbon upgrading processes used petroleum refining and petrochemical applications. These processes include hydrocracking (MPHC) for maximum distillate production. It has, however, been found that high silica zeolites typically exhibit an
10 increase in acid activity when bound with alumina. Activation of the zeolite by the alumina binder has been attributed to alumina incorporation into the zeolite framework which decreases the silica/alumina ratio and increases the zeolite acidity, as disclosed by C.D. Chang,
15 S.D. Hellring, J.N. Miale, K.D. Schmitt, P.W. Brigandi, and E.L. Wu in J. Chem. Soc., Faraday Trans., I, 81, 2215 (1985).

In many cases this activation has a detrimental impact on catalyst performance. For example, the performance of
20 VGO hydrocracking catalysts comprised of large-pore zeolites disclosed in U.S. Pat. No. 4,820,402 demonstrates a unique relationship between selectivity to high value middle distillate products and increasing zeolite silica/alumina ratio. Furthermore, the occurrence of
25 alumina binder activation in zeolites and the extent to which it occurs have been difficult to predict.

Binding the zeolites with silica, as disclosed in U.S. Pat. No. 4,582,815, is currently one of the preferred methods of eliminating this binder activation. In some
30 applications, however, silica binding may not be applicable such as with bi-functional hydrocracking catalysts where a metal component must be dispersed on the binder. It would be desirable, therefore, to develop a procedure for preparing stable, low acidity zeolites in alumina binder.

This present invention seeks to provide a process for the preparation of high silica zeolite catalysts with improved resistance to alumina binder activation.

Accordingly, the invention resides in a process for preparing an alumina bound zeolite catalyst, comprising the steps of:

- (a) starting with a zeolite which has a silanol content of less than 10%, expressed in terms of silicon atoms containing silanol groups vs. total silicon atoms;
- (b) mulling together alumina, said zeolite of step (a), and water to form an extrudable mass comprising an intimate mixture of alumina and said zeolite;
- (c) extruding the extrudable mass of step (b) to form a green strength extrudate; and
- (d) calcining the green strength extrudate of step (c) to increase the crush strength of the extrudate.

The invention further provides a process for hydrocracking a hydrocarbon feedstock, said process comprising contacting said feedstock and hydrogen with a hydrocracking catalyst comprising a hydrogenation component and an extrudate prepared according to the above-mentioned process.

The present invention provides a process for preparing zeolite catalysts that enables low acidity, high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio zeolites to be stabilized toward increases in acid activity that arise from aluminum incorporation into the framework during the alumina binding procedure. The catalysts may be prepared from zeolites subjected to a thermal and/or hydrothermal treatment to reduce crystal defect sites, such as silanol groups, prior to contact with the alumina binder.

The procedure may involve a zeolite treatment, such as mild steaming, to effect a reduction in structural defect

-4-

sites within the zeolite, such as zeolite silanol groups, prior to contact with the alumina binder.

Previous investigators have identified defect sites, such as silanols, in high silica zeolites, such as ZSM-5, using FT-IR and ^{29}Si MAS NMR as described by R.M. Dessau, K.D. Schmitt, G.T. Kerr, G.L. Woolery, and L.B. Alemany in J. Catal., 104, 484 (1987). Hydrothermal treatment reduces the silanol content in ZSM-5 and this has been interpreted to occur through a silanol annealing mechanism. However, the relationship between zeolite silanol content and binder activation, and the necessity to control zeolite silanol content prior to contact with the alumina binder has heretofore not been recognized.

The present process first involves combining alumina, zeolite and water in a mulling procedure. The amount of alumina should be sufficient to provide the required crush strength to the ultimately produced extrudate and typically will be 5-95 wt%, preferably 20-80 wt.%, on a 100% solids basis. The amount of zeolite will be dependent on the required catalytic activity to the ultimately produced catalyst and again will typically be 5-95 wt%, preferably 20-80 wt.%, on a 100% solids basis. A sufficient amount of water should be added to provide adequate extrudability to the solids in the mixture. For example, the amount of water may be 40-50 wt.% of the solids. This extrudable mixture may be in the form of a paste.

The alumina which is used to form this extrudable mixture may be in the form of a hydrated alumina, such as pseudoboehmite.

The zeolite, which is used to form the extrudable mass with alumina and water, has a low silanol content. This silanol content may be less than 10%, e.g., less than 5%, expressed in terms of silicon atoms containing silanol groups vs. total silicon atoms. These percentages of silanol content may be determined by ^{29}Si MAS NMR. Silicon-29 NMR is an effective tool to determine the

silanol content. A ^{29}Si NMR spectrum of a high-silica zeolite typically exhibits three Si species corresponding to framework Si, silanol (SiOH), and diol ($\text{Si}(\text{OH})_2$). By integrating the areas of these peaks, the silanol content can be determined. The method is described by E. Lippmaa, M. Maegi, A. Samoson, M. Tarmamak, and G. Engelhardt in the J. Am. Chem. Soc. **103**, 4992, (1981). Other techniques that can measure silanol content semi-quantitatively, including FT-IR and proton NMR, can also be used.

It will be understood that, whenever the silanol content of a zeolite is referred to herein, this silanol content is attributed exclusively to silanols which are part of the zeolite framework and excludes non-framework silanols, such as those which may be present from amorphous silica impurities and/or occlusions, e.g., carried over from the reaction mixture used to prepare the zeolite.

Zeolites which may be used to form catalysts by methods disclosed herein include medium-pore size and large-pore size zeolites.

A convenient measure of the extent to which a zeolite provides control of access to molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. Zeolites which provide a highly restricted access to an egress from its internal structure have a high value for the Constraint Index, and zeolites of this kind usually have pores of small size, e.g., less than 5 Angstroms. On the other hand, zeolites which provide relatively free access to the internal zeolite structure have a low value for the Constraint Index, and usually pores of large size, e.g., greater than 8 Angstroms. The method by which Constraint Index is determined is described fully in U.S. Patent No. 4,016,218, incorporated herein by reference for details of the method.

A zeolite which may be used in catalyst preparation described herein may be a medium- or large-pore size zeolite. This zeolite may have a Constraint Index of 12 or

less. Zeolites having a Constraint Index of 2-12 are generally regarded to be medium-pore size zeolites.

Zeolites having a Constraint Index of less than 1 are generally regarded to be large-pore size zeolites.

- 5 Zeolites having a Constraint Index of 1-2 may be regarded as either medium- or large-pore size zeolites.

The members of the class of medium-pore size zeolites may have an effective pore size of generally from about 5 to about 8 Angstroms, such as to freely sorb normal hexane.

- 10 In addition, the structures provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum
15 atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the medium-pore size type. Windows of 10-membered rings are preferred, although, in some instances, excessive puckering of the rings or pore blockage may render these
20 zeolites ineffective.

- Although 12-membered rings in theory would not offer sufficient constraint to constitute a medium-size pore, it is noted that the puckered 12-ring structure of TMA
offretite does show some constrained access. Other 12-ring
25 structures may exist which may be regarded to be medium-pore sized, and therefore, it is not the present intention to classify a particular zeolite solely from theoretical structural considerations.

- 30 Constraint Index (CI) values for some typical materials are:

-7-

<u>CI (at test temperature)</u>			
	ZSM-4	0.5	(316°C)
	ZSM-5	6 - 8.3	(371°C-316°C)
	ZSM-11	5 - 8.7	(371°C-316°C)
5	ZSM-12	2.3	(316°C)
	ZSM-20	0.5	(371°C)
	ZSM-22	7.3	(427°C)
	ZSM-23	9.1	(427°C)
	ZSM-34	50	(371°C)
10	ZSM-35	4.5	(454°C)
	ZSM-38	2	(510°C)
	ZSM-48	3.5	(538°C)
	ZSM-50	2.1	(427°C)
	TMA Offretite	3.7	(316°C)
15	TEA Mordenite	0.4	(316°C)
	Mordenite	0.5	(316°C)
	Clinoptilolite	3.4	(510°C)
	Mordenite	0.5	(316°C)
	REY	0.4	(316°C)
20	Amorphous Silica-alumina	0.6	(538°C)
	Dealuminized Y (Deal. Y)	0.5	(510°C)
	Erionite	38	(316°C)
	Zeolite Beta	0.6 - 2.0	(316°C-399°C)

25 Examples of zeolites having a Constraint Index of from 1 to 12 include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, and ZSM-48.

ZSM-5 is described U.S. Patent Nos. 3,702,886 and Re. 29,948.

30 ZSM-11 is described in U.S. Patent No. 3,709,979.
 ZSM-12 is described in U.S. Patent No. 3,832,449.
 ZSM-22 is described in U.S. Patent No. 4,556,477.
 ZSM-23 is described in U.S. Patent No. 4,076,842.
 ZSM-35 is described in U.S. Patent No. 4,016,245.
 ZSM-38 is described in U.S. Patent No. 4,406,859.
 35 ZSM-48 is described in U.S. Patent No. 4,234,231

Examples of large-pore zeolites, having a Constraint Index less than 1 include Zeolite Beta, Zeolite Y, Ultrastable Y (USY), Dealuminized Y (Deal Y), Mordenite, ZSM-3, ZSM-4, ZSM-10, ZSM-18, and ZSM-20.

5 Zeolite Beta is described in U.S. Patent No. 3,308,069 and Re. No. 28,341.

ZSM-4 is described in U.S. Patent No. 3,923,639.

ZSM-10 is described in U.S. Patent No. 3,692,470.

ZSM-20 is described in U.S. Patent No. 3,972,983.

10 Low sodium Ultrastable Y molecular sieve (USY) is described in U.S. Patent Nos. 3,293,192 and 3,449,070.

Dealuminized Y zeolite (Deal Y) may be prepared by the method found in U.S. Patent No. 3,442,795.

15 Zeolite UHP-Y is described in U.S. Patent No. 4,401,556.

Another zeolite which may be used in the present catalyst is MCM-22, which is described in U.S. Patent Nos. 4,954,325 and 5,107,054.

20 A particularly preferred zeolite for use in the present catalyst is zeolite Y.

Zeolite Y is normally synthesized in forms having silica:alumina ratios up to about 5:1. These as-synthesized forms of zeolite Y may be subjected to various treatments to remove structural aluminum therefrom. Many of these techniques rely upon the removal of aluminum from the structural framework of the zeolite by chemical agents appropriate to this end. A considerable amount of work on the preparation of aluminum deficient faujasites has been performed and is reviewed in Advances in Chemistry Series
30 No. 121, Molecular Sieves, G.T. Kerr, American Chemical Society (1973). Specific methods for preparing dealuminized zeolites are described in the following, and reference is made to them for details of the method:
Catalysis by Zeolites, International Symposium on Zeolites,
35 Lyon, Elsevier Scientific Publishing Co., (1980)
(dealuminization of zeolite Y with silicon tetrachloride);

U.S. Pat. No. 3,442,795 and G.B. No. 1,058,188 (hydrolysis and removal of aluminum by chelation); G.B. No. 1,061,847 (acid extraction of aluminum); U.S. Pat. No. 3,493,519 (aluminum removal by steaming and chelation); U.S. Pat. No. 3,591,488 (aluminum removal by steaming); U.S. Pat. No. 4,273,753 (dealuminization by silicon halide and oxyhalides); U.S. Pat. No. 3,691,099 (aluminum extraction with acid); U.S. Pat. No. 4,093,560 (dealuminization by treatment with salts); U.S. Pat. No. 3,937,791 (aluminum removal with Cr(III) solutions); U.S. Pat. No. 3,506,400 (steaming followed by chelation); U.S. Pat. No. 3,640,681 (extraction of aluminum with acetylacetonate followed by dehydroxylation); U.S. Pat. No. 3,836,561 (removal of aluminum with acid); DE-OS No. 2,510,740 (treatment of zeolite with chlorine or chlorine-containing gases at high temperatures); NL No. 7,604,264 (acid extraction); JA No. 53,101,003 (treatment with EDTA or other materials to remove aluminum); and J. Catal. 54, 295 (1978) (hydrothermal treatment followed by acid extraction).

Highly siliceous forms of zeolite Y may be prepared by steaming or by acid extraction of structural aluminum but because zeolite Y in its normal, as-synthesized condition, is unstable to acid, it must first be converted to an acid-stable form. Methods for doing this are known and one of the most common forms of acid-resistant zeolite Y is known as "Ultrastable Y" (USY); it is described in U.S. Pat. Nos. 3,293,192 and 3,402,996 and the publication, Society of Chemical Engineering (London) Monograph Molecular Sieves, 186 (1968) by C.V. McDaniel and P.K. Maher. In general, "ultrastable" refers to Y-type zeolite which is highly resistant to degradation of crystallinity by high temperature and steam treatment and is characterized by a R_2O content (wherein R is Na, K or any other alkali metal) of less than 4 weight percent, preferably less than 1 weight percent, and a unit cell size less than 24.5 Angstroms and a silica to alumina mole ratio in the range

-10-

of 3.5 to 7 or higher. The ultrastable form of Y-type zeolite is obtained primarily by a substantial reduction of the alkali metal ions and the unit cell size. The ultrastable zeolite is identified both by the smaller unit cell and the low alkali metal content in the crystal structure.

The ultrastable form of the Y-type zeolite can be prepared by successively base exchanging a Y-type zeolite with an aqueous solution of an ammonium salt, such as ammonium nitrate, until the alkali metal content of the Y-type zeolite is reduced to less than 4 weight percent. The base exchanged zeolite is then calcined at a temperature of 540°C to 800°C for up to several hours, cooled and successively base exchanged with an aqueous solution of an ammonium salt until the alkali metal content is reduced to less than 1 weight percent, followed by washing and calcination again at a temperature of 540°C to 800°C to produce an ultrastable zeolite Y. The sequence of ion exchange and heat treatment results in the substantial reduction of the alkali metal content of the original zeolite and results in a unit cell shrinkage which is believed to lead to the ultra high stability of the resulting Y-type zeolite.

The ultrastable zeolite Y may then be extracted with acid to produce a highly siliceous form of the zeolite.

Other methods for increasing the silica:alumina ratio of zeolite Y by acid extraction are described in U.S. Pat. Nos. 4,218,307; 3,591,488 and 3,691,099.

In addition to the above-mentioned USY form of zeolite Y, other known forms of zeolite Y, including the rare earth exchanged Y form (REY), may be used in the present catalyst.

The zeolite Y used in the present catalyst may have a unit cell size (UCS) of, for example, 24.5 Angstroms or less, typically 24.15-24.50 Angstroms. Such zeolites

having a low UCS, e.g., of 24.15-24.30 Angstroms, may be particularly advantageous.

Zeolite Y with a low silanol content may be manufactured or obtained directly from commercial vendors.

5 The silanol content of zeolites can be adjusted by various treatments including synthesis, thermal or hydrothermal treatments as described in the previously cited literature.

The extrudable mass may be passed through an extrusion die under conditions sufficient to form cylindrical
10 extrudates, which may, in turn, be broken into pellets.

The strength of the extrudate pellets may ultimately be increased to optimum levels by a calcination procedure. However, the uncalcined extrudate has sufficient green strength to withstand the usual handling procedures, which
15 involve drying and possibly ion exchanging and/or impregnating with sources of hydrogenation components. Drying of the extrudate pellets may take place at temperatures of from 100°C to 150°C. This drying procedure removes water which is physically included or associated
20 with the extrudate. Further water, termed chemically bound water, may be removed from the extrudate upon calcination at higher temperatures.

The crush strength of the green strength extrudate material is improved by a calcination step. This
25 calcination may take place at a sufficient temperature, e.g., greater than 400°C, for a sufficient time, e.g., at least 1 hour, in an appropriate atmosphere, e.g., nitrogen or air. This calcination may cause phase transformation of the alumina binder to occur. More particularly, the
30 alumina binder may be transformed into the form of gamma-alumina during this calcination step.

The extrudate catalyst may be combined with a hydrogenation component or a source of a hydrogenation component either before or after the calcination step. Th
35 hydrogenation component may be a hydrogenation metal which may be a noble metal or metals, or a n n-noble metal or

metals. Suitable noble metals include platinum, palladium, and other members of the platinum group such as iridium and rhodium. Suitable non-noble metals include those of Groups VA, VIA and VIIIA of the Periodic Table. The Periodic Table used in this specification is the table approved by IUPAC and the U.S. National Bureau of Standards, as shown for instance in the table of the Fisher Scientific Company, Catalog No. 5-702-10. Preferred non-noble metals are molybdenum, tungsten, cobalt and nickel and combinations of these metals such as cobalt-molybdenum, nickel-molybdenum, nickel-tungsten and cobalt-nickel-tungsten. Metal components may be pre-sulfided prior to use by exposure to a sulfur-containing gas such as hydrogen sulfide at an elevated temperature to convert the oxide form to the corresponding sulfide form of the metal.

The metal may be incorporated into the catalyst by any suitable method such as impregnation or exchange onto the extrudate. The metal may be incorporated in the form of a cationic, anionic or neutral complex such as $\text{Pt}(\text{NH}_3)_4^{2+}$ and cationic complexes of this type will be found convenient for exchanging metals onto the zeolite. Anionic complexes such as the molybdate or metatungstate ions are useful for impregnating metals into the catalysts.

The amount of the hydrogenation metal is suitably from 0.01 to 30 percent by weight, normally 0.1 to 20 percent by weight based on the weight of the zeolite and matrix plus the weight of the hydrogenation metal, although this will, of course, vary with the nature of the component, less of the highly active noble metals, particularly platinum, being required than of the less active base metals.

The catalyst of the invention is particularly useful in hydrocracking, which is typically carried out at a temperature ranging from 250°C (480°F) to 500°C (930°F), preferably from 300°C (570°F) to 450°C (840°F); a hydrogen pressure ranging from 2 to 21 MPa; a liquid hourly space velocity ranging from 0.05 to 10, preferably from 0.2 to 3;

-13-

a H_2 circulation ranging from 90 to 1780 Nm^3/m^3 (500 to 10,000 scfb), preferably from 360 to 1070 Nm^3/m^3 (2000 to 6000 scfb).

The conversion may be conducted by contacting the feedstock with a fixed stationary bed of catalyst, a fixed fluidized bed or with a transport bed. A simple configuration is a trickle-bed operation in which the feed is allowed to trickle through a stationary fixed bed. With such a configuration, it is desirable to initiate the reaction with fresh catalyst at a moderate temperature which is of course raised as the catalyst ages, in order to maintain catalytic activity.

The catalyst of the invention may be used to hydrocrack a variety of feedstocks such as crude petroleum, reduced crudes, vacuum tower residua, coker gas oils, cycle oils, FCC tower bottoms, vacuum gas oils, deasphalted residua and other heavy oils. These feedstocks may optionally be subjected to a hydrotreating treatment prior to being subjected to the present hydrocracking process. The feedstock, especially in the non-hydrotreated form, will contain a substantial amount boiling above 260°C (500°F) and will normally have an initial boiling point of about 290°C (about 550°F) more usually about 340°C (650°F). Typical boiling ranges will be about 340°C to 565°C (650°F to 1050°F). Heavy gas oils are often of this kind as are cycle oils and other non-residual materials. Oils derived from coal, shale or tar sands may also be treated in this way. It is possible to co-process materials boiling below 260°C (500°F) but they will be substantially unconverted. Feedstocks containing lighter ends of this kind will normally have an initial boiling point above 150°C (about 300°F). Feedstock components boiling in the range of 290° to 340°C (about 550° to 650°F) can be converted to products boiling from 230°C to 290°C (about 450° to 550°F) but the heavier ends of the feedstock are converted preferentially to the more volatile components and therefore the lighter

ends may remain unconverted unless the process severity is increased sufficiently to convert the entire range of components. A particular hydrocarbon feedstock which may be used is an FCC recycle oil having an initial boiling point of at least about 343°C (650°F). Other examples of feedstocks include those with relatively large contents of non-aromatic hydrocarbons, such as paraffinic feedstocks, e.g., feedstocks having at least 20 percent by weight, e.g., at least 50 percent by weight of paraffins.

Feedstocks, including those which have been hydrotreated, which may be used in the present process, include those having at least 70 wt.% of hydrocarbons having a boiling point of at least 204°C (400°F).

The hydrocarbon feedstock for the hydrocracking process may be a gas oil. This gas oil may have an initial boiling point of at least 260°C (500°F), and at least 90 wt.% of the hydrocarbons therein may have a boiling point greater than 343°C (650°F). This hydrocracking process involving a gas oil feed may involve a net production of a distillate fraction. For example, the product of the hydrocracking reaction may have at least 25 wt.% of hydrocarbons having a distillate boiling range of from 165 to 343°C (330°F to 650°F). The distillate fraction may be recovered, preferably by a fractional distillation process.

Example 1

Preparation of High Silica, Low Silanol USY Catalyst Catalyst A

A commercial high silica USY zeolite containing essentially no silanol groups as determined by Si-NMR was milled in a 50/50 wt/wt. mixture with alumina and extruded to prepare a formed mass. The extruded mass was dried at 120°C (250°F) and calcined for 3 hours in 5 v/v/min. flowing air at 540°C (1000°F). The calcined product was

-17-

included temperatures from 715-765°F (about 380-410°C), 0.5 LHSV (based on fresh feed relative to total HDT and HDC catalyst), 4000 scf/bbl (712 n.l.l.⁻¹) of once-through hydrogen circulation, and hydrogen inlet pressure of 815 psia (5.61 MPa). The ratio of HDT to HDC catalyst was typically 1/2, vol/vol.

The feedstock for this Example was a nominal 650-1050°F (about 345-565°C) Persian Gulf VGO (vacuum gas oil) having the properties shown in Table 2 below.

10

Table 2**Persian Gulf VGO Feedstock Properties**General Properties

API Gravity	22.0
Hydrogen, wt.%	12.53
15 Sulfur, wt.%	2.53
Nitrogen, ppm	780
Pour point, °F	100
KV @ 40°C, cSt.	74.34
KV @ 100°C, cSt.	7.122

20

Composition, wt.%

Paraffins	24.1
Naphthenes	22.1
Aromatics	53.8

Distillation, °F (°C)

25	IBP	546 (286)
	5%	627 (331)
	10%	664 (351)
	30%	760 (404)
	50%	831 (444)
30	70%	906 (486)
	90%	1003 (539)
	95%	1041 (561)
	EP	1158 (626)

Table 3 shows the improved performance of Catalyst A prepared from low silanol USY compared to Catalyst B. At

35

-18-

equivalent 343°C+ (650°F+) boiling range conversion, Catalyst A provides higher yield of valuable distillate product (165-343°C) with lower yield of light gas (C₁-C₄) and naphtha (C₅-165°C). Hydrogen consumption is lower due to reduced light gas product. Distillate selectivity, defined as distillate yield/343°C+ conversion, is 4% higher for Catalyst A.

Table 3**Hydrocracking Performance with Persian Gulf VGO**

		<u>Catalyst A</u>	<u>Catalyst B</u>
10	Temperature, °F	755	765
	°C	402	407
	650°F+ Conversion, wt.%	40.9	40.7
	<u>Yields, wt.%</u>		
15	H ₂ S	2.5	2.7
	NH ₃	0.1	0.1
	C ₁ -C ₄	2.0	2.5
	C ₅ -330°F (165°C)	8.7	9.9
	330-650°F (145-343°C)	32.7	31.0
20	650°F+ (343°C)	54.7	54.9
	H ₂ Consumption, scf/bbl	430	570
	(Nm ³ /m ³)	76.5	101.5
	Distillate Selectivity	80%	76%
25	(Distillate yield/ (650°F) 343°C conversion)		

Claims:

1. A process for preparing an alumina b und zeolite catalyst, comprising the steps of:
 - (a) starting with a zeolite which has a silanol content of less than 10%, expressed in terms of silicon atoms containing silanol groups vs. total silicon atoms;
 - (b) mulling together alumina, said zeolite of step (a), and water to form an extrudable mass comprising an intimate mixture of alumina and said zeolite;
 - (c) extruding the extrudable mass of step (b) to form a green strength extrudate; and
 - (d) calcining the green strength extrudate of step (c) to increase the crush strength of the extrudate.
2. A process according to claim 1, wherein said green strength extrudate is calcined at a temperature of at least 400°C in calcination step (c).
3. A process according to claim 1 or claim 2, wherein said alumina, which is introduced into mulling step (a), is in the form of pseudoboehmite.
4. A process according to any preceding claim, wherein said green strength extrudate of step (b) is dried to remove physically included water therefrom prior to calcination step (c).
5. A process according to claim 5, wherein the drying of the extrudate prior to step (c) takes place at a temperature of 100°C to 150°C.
6. A process according to any preceding claim, wherein said zeolite is a large-pore size zeolite.